

AIRBORNE OBSERVATIONS OF THE COMPOSITION OF THE 1992 TROPICAL STRATOSPHERE BY FTIR SOLAR ABSORPTION SPECTROMETRY

G.G. Toon, J.-P. Blavier, J.N. Solario, and J.T. Szeto

Jet Propulsion Laboratory, California Institute of Technology

Abstract. Vertical column measurements of the gaseous composition of the tropical stratosphere were made from the NASA DC-8 aircraft early in 1992. As anticipated, the burdens of the stratospheric source gases (e.g. O_3 , HF , HCN , $ClNO_2$, and INO_2) were reduced from their mid-latitude values due to increased uplift and photolysis. The tracers revealed considerably more uplift near the equator than the sub-tropics. For example, the HF burdens at $\pm 200^\circ$ latitude (0.5×10^{15} molec. cm^{-2}) were 1 km² 1% double those at $5^\circ N$ (0.27×10^{15} molec. cm^{-2}). This, together with results obtained from other long-lived gases (e.g. N_2O , CH_4 , CF_2Cl_2) indicates that volume mixing ratios found at 22 km altitude at mid-latitudes occurred at 26 km in the sub-tropics and at 30 km in the equatorial zone. This zone of uplift was symmetrical about the equator even though the sun was overhead at 200° .

Observations

The JPL Mk1 V interferometer, a Fourier Transform Infrared (FTIR) spectrometer purpose-built for atmospheric remote measurements (Toon, 1991), was one of twelve instruments installed on the NASA DC-8 aircraft to participate in the second Airborne Arctic Stratosphere Experiment (AASE II). During this three month campaign, 19 flights were conducted, the majority over the Arctic region (Toon et al., 1992c). Four flights were made to lower latitudes in order to assess the impact of the Pinatubo eruption on the composition of the tropical stratosphere. The locations of those observations are illustrated in Figure 1.

It should be stated at the outset that tropical measurements using the solar absorption technique are more difficult to make than those at higher latitudes. The optimal solar zenith angle for this type of stratospheric observation is 85° to 88° . Unfortunately, observed from a sub-sonic aircraft, the tropical sun takes only a few minutes to pass through this optimal range of zenith angles. By contrast, at high latitudes the sun may be held in the optimal range for hours by careful choice of flight path. The short tropical sunset/rise transitions

Fig. 1

reduced the detectability of some gases, giving rise to larger errors than in comparable measurements at high latitudes.

The quality of the tropical data was further degraded by the presence of cirrus cloud above the aircraft. At higher latitudes the DC-8 aircraft, which cruises at about 11 km altitude, can nearly always fly above the tropopause and its associated cirrus, but in the tropics it is always well below. The presence of cirrus was detrimental not just because it attenuated the direct solar radiation reaching the instrument, but mainly because structure in the cirrus caused intensity fluctuations. Since these fluctuations were generally faster than the time (50 s) required to record a single interferogram, they distorted the depths and shapes of spectral lines in the derived spectrum, causing greater uncertainty in the burdens.

Data Reduction

Each individual spectrum covered the entire 650-5400 cm^{-1} spectral region simultaneously at 0.02 cm^{-1} resolution (30 cm optical path difference). Spectra were averaged in groups of 4 to 8 before analysis. Each averaged spectrum therefore represents 3-6 minutes of observation. Averaging reduces the labor of analysis and provides a smaller uncertainty in the retrieved burdens.

The data were analyzed by the same method as was described by Toon et al. (1992a): A least squares spectral fitting algorithm adjusted the assumed volume mixing ratio (vmr) profile of the gas of interest until the line-by-line calculation best matched the observed spectrum. The precision of the retrieved burdens was then estimated from the quality of the spectral fit. For many of these gases multiple spectral intervals were used to determine the amount of gas (e. g. for HCl five separate lines were used), in which case the value in Table 1 is the weighted mean.

Discussion

Since the vmr profile of CO_2 is almost constant and accurately known throughout the troposphere and stratosphere, its burden can be accurately predicted. Thus, our measured CO_2 burdens can be used to test for the presence of systematic effects, such as errors in the observation geometry, or the assumed temperature profiles. Figure 2a shows the mean (pressure-weighted) CO_2 vmr above the aircraft, obtained by dividing the burdens in Table 1 by the observation pressure. The average value was about 355 ppmv, a value consistent

Table 1

Fig. 2

with in situ measurements e.g. Schmidt and Khedim (1991). Despite the variability at 26°-27°N (Jan.9) which exceeds the measurement precision, the rms scatter of the CO₂ is still only about 2%. For the other gases (but not CO₂) the major source of systematic error was the shape of their vmr profile, which can give rise to an error as large as 8% at the highest solar zenith angles.

Figure 2b shows the H₂O vmr above the aircraft. The observations north of 25°N were made above the tropopause and show the typical lower stratospheric vmr of about 4 ppmv. The observations south of 25°N were made from below the tropopause and so reflect the much larger tropospheric H₂O amounts. The abrupt drop in the amount of H₂O at 200° marks our emergence from a large region of numerous cumulonimbus clouds into clear sky.

Transport. The H₂ burdens reported in Table 1 are much larger than previous tropical measurements but this is likely due to the 10% annual H₂ increase (WMO, 1986). Perhaps the most interesting feature exhibited by H₂ is the small size of the equatorial burdens compared with those in the subtropics. The main reason for this is that upwelling causes advection of H₂-poor tropospheric air into the lower stratosphere. The same upwelling has the opposite effect on tropospheric source gases. The observed enhancements of equatorial HCN, N₂O, CH₄, CF₂Cl₂ and CFCl₃ burdens are quantitatively consistent with each other and with the loss of H₂, although this is not immediately apparent from Table 1 due to the fact that differences in the aircraft altitude mask the latitudinal variations of the tropospheric source gases. To minimize such artifacts, the burdens of these gases were retrieved not by scaling the assumed vmr profile, but by squashing it in the vertical (see Toon et al., 1992b) according to the equation

$$\text{vmr}(z) = \text{vmr}(z(1+\text{DOS}))$$

Values for the Degree of Subsidence (DOS) were derived for each spectrum by averaging the results obtained from H₂, N₂O, CH₄, and CF₂Cl₂. Of course, the DOS values reported in Table 1 are somewhat arbitrary depending on the initial reference profiles, which were mid-latitude vmrs stretched in the vertical so as to give DOS values of around zero in the tropics. DOS increased with latitude, to 0.15 in the subtropics, and 0.36 at mid-latitudes, indicating that vmrs found at 30 km altitude near the equator would be found at 26 km

in the subtropics and at 22 km at mid-latitudes. Figure 3 illustrates the consistency in the vertical shifts derived from those different tracers, and also illustrates that their gradient is greater in the subtropics than at mid-latitudes. A large gradient is indicative of a stratospheric barrier to latitudinal transport, such as occurs at the edge of the polar vortices. This barrier seems underestimated in current circulation models. For example, Kaye et al. (1991) predicted that the HCl burdens in the $30\text{--}37^\circ$ latitude range should be double those at the equator. Our results (Figure 4a) show that doubling occurred by 22° .

[Fig. 3]

Chemical Partitioning. Figure 4b shows the measured HCl burdens. While the latitudinal variation is qualitatively similar to previous measurements (Mankin and Coffey, 1983; Girard et al., 1983; and Karcher et al., 1988), our HCl amounts are higher, a probable consequence of the 5% annual HCl increase. Our measured HO/HCl ratio increased from around 3.3 at mid-latitude to 4.7 in the tropics. This is consistent with the idea (Kaye et al., 1991) of a greater fraction of tropical inorganic fluorine being in the form of COF_2 and COFCl rather than HCl , and so should not be interpreted as evidence of volcanic injection of HCl from the Pinatubo eruption.

[Fig. 4]

As expected, the equatorial ClNO_2 burdens ($0.55 \pm 0.20 \times 10^{15} \text{ molec.cm}^{-2}$), calculated as the weighted average of the values in Table 1, were smaller than those observed in the subtropics (0.70 ± 0.20) or mid-latitudes (1.20 ± 0.20). HOCl was not detectable in any of the tropical spectra, but values were included in Table 1 to provide upper limits.

Our observed HNO_3 burdens (Figure 4c) are broadly consistent with the previous low latitude measurements of Karcher et al. (1988), Coffey et al. (1981) and Girard et al. (1983), but not the very low ($0.9 \pm 0.2 \times 10^{15} \text{ molec.cm}^{-2}$) burden measured by Karcher et al. (1988) at 10°S in June 1984. Our HNO_3 burdens at $\pm 20^\circ$ latitude were almost identical at $6.1 \times 10^{15} \text{ molec.cm}^{-2}$ despite the sun being overhead at 20°S and were more than double those found near the equator. Since the contrast between the equatorial and the subtropical HNO_3 burdens is greater than that of HCl , one might argue that photolysis of equatorial HNO_3 augments the loss due to uplift. However, since the sun was overhead at 20°S , uplift must nevertheless play the dominant role in defining the latitudinal distribution of HNO_3 .

Our tropical NO_2 burdens (Figure 4d) were somewhat lower than pre-Pinatubo measurements, presumably a consequence of heterogeneous conversion of N_2O_5 to HNO_3 on Pinatubo

aerosol, but not the factor 2 seen at mid-latitude sunrises (T'0011 et al., 1992c; Johnston et al., 1992). This is to be expected since the faster rate of HNO_3 photolysis in the tropics would reduce the impact of heterogeneous production. Our sunset NO_2 burdens ($1.78 \times 10^{15} \text{ molec.cm}^{-2}$) observed at $4^\circ\text{--}8^\circ\text{N}$ are lower than any previous tropical sunset results. For example, $2.9 \times 10^{15} \text{ molec.cm}^{-2}$ was measured in June 1978 by Coffey et al (1981), and $1.95 \times 10^{15} \text{ molec.cm}^{-2}$ was measured in June 1984 by Karcher et al. (1988). The diurnal cycle of NO and NO_2 makes it difficult to ascertain their true latitudinal variation. However, at sunset there was certainly 20% less NO and NO_2 in the equatorial zone (2.7 & $1.8 \times 10^{15} \text{ molec.cm}^{-2}$ respectively) than at 20°N (3.3 & $2.2 \times 10^{15} \text{ molec.cm}^{-2}$ respectively), a result consistent with previous measurements (WMO, 1986).

Ozone burdens were fairly constant across the entire tropics and subtropics at about 6.2×10^{15} (230 Dobson Units). The fact that ozone was not reduced by uplift in the equatorial zone like H_2O or HNO_3 indicates that the timescale of its formation was faster than that of the upward motion, so that ozone was able to re-establish its chemical equilibrium. While in situ measurements of tropical ozone (Grant et al., 1992) revealed decreases as large as 20% in the 20-30 km altitude range following the Pinatubo eruption, increases above and below these altitudes ameliorated the total perturbation to the ozone burden to less than 5%. Given the sparsity of our measurements, it is not surprising that we cannot confirm a 5% tropical total ozone loss.

Summary

The 1992, equatorial lower stratosphere was uplifted some 4 km with respect to the sub-tropics. Since previous tropical measurements (by other instruments) show large scatter we cannot say whether this amount of uplift is normal or was augmented from heating by Pinatubo aerosol. This uplift appeared to be symmetrical about the equator, despite the sun being overhead at 20°S , indicating that it is not directly driven by solar heating. Apart from slightly reduced NO and NO_2 burdens, the partitioning of the chemically active species appeared normal, with no evidence of heterogeneous chemical reactions involving chlorine.

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J.-F. Blavier, J. N. Solaro, J.T. Szeto, and G. C. Toon, Jet Propulsion Laboratory, MS 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

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Fig. 1. Locations of the observations discussed in this paper: Jan. 8 sunset (cross), Jan. 11 sunrise (diamond), Jan. 28 sunrise (circle), Jan. 30 sunset (square), and Feb. 20 sunset (triangle).

Fig. 2. Mean vmrs of CO₂ and H₂O above the aircraft.

Fig. 3. Vertical shifts of the reference vmr profiles required to match observed spectral absorption features: HF (Y symbol), N₂O (Z symbol), Cl₂ (bow-tie), and Cl₂Cl₂ (hour-glass).

Fig. 4. Latitudinal variations of the burdens (molec.cm⁻²) of HF, HCl, HNO₃, and NO₂.

Table 1. Summary of observations discussed in the paper. DOY is the fractional day of the year (e.g. 9.050 is 01:12 UT on January 9th). Lat. is the latitude, and Lon. is the longitude.

θ is the solar zenith angle (degrees). P and T are the pressure (mbar) and temperature (K) outside the aircraft at the time of each observation. 1) OS is the degree of subsidence (see text).

The second row contains the exponents of the multipliers to be applied to the values below them. The remainder of the table contains the measured burdens of each gas (molec.cm⁻²).

DOY	Lat.	Lon.	θ	P	T	DOS	CO ₂	HCN	CH ₄	N ₂ O	OCS	CF ₂ C ₁₂	CFCl ₃	HF	HCl
0	0	0	0	0	0	0	21	15	18	18	15	15	15	15	15
09.050	26.6	-122.6	86.6	188.9	222.9	0.28	1.36±.05	1.04±.13	5.87±.10	0.99±.02	1.60±.07	1.01±.04	0.77±.04	0.66±.06	1.93±.15
09.054	27.1	-122.8	87.5	175.9	220.6	0.23	1.32±.04	0.93±.10	5.53±.08	0.94±.02	1.49±.07	0.96±.02	0.75±.02	0.65±.05	2.03±.14
09.057	27.5	-123.1	88.5	175.9	220.5	0.21	1.36±.04	0.97±.09	5.57±.08	0.96±.02	1.58±.05	0.96±.02	0.75±.02	0.67±.06	1.95±.13
11.673	47.4	-118.3	86.5	176.1	227.4	0.35	1.33±.04	0.65±.10	5.14±.06	0.83±.01	1.23±.05	0.83±.02	0.56±.01	0.91±.05	2.93±.13
11.676	47.0	-118.7	85.9	176.0	227.6	0.35	1.31±.04	0.67±.11	5.04±.07	0.83±.01	1.25±.06	0.83±.03	0.55±.02	0.90±.05	2.98±.13
11.688	45.2	-120.5	83.4	176.1	227.4	0.36	1.31±.03	0.65±.10	5.07±.06	0.83±.01	1.28±.06	0.81±.03	0.52±.02	0.87±.04	2.97±.11
11.695	44.2	-121.4	81.9	175.9	225.7	0.37	1.31±.03	0.61±.10	5.11±.06	0.82±.01	1.30±.07	0.80±.03	0.53±.03	0.91±.04	3.09±.09
28.669	-19.2	-149.5	85.5	175.8	214.6	0.15	1.31±.04	0.37±.13	5.66±.08	0.99±.01	1.61±.06	1.06±.02	0.94±.02	0.45±.04	1.75±.12
28.675	-20.1	-149.7	83.8	175.8	214.6	0.16	1.34±.07	0.45±.23	5.89±.14	1.00±.02	1.64±.10	1.02±.04	0.89±.04	0.48±.08	1.82±.23
28.682	-21.5	-149.9	81.2	175.8	214.7	0.18	1.34±.03	0.51±.11	5.76±.06	0.99±.01	1.60±.07	1.02±.05	0.85±.05	0.52±.03	1.91±.08
30.085	04.4	-130.6	79.1	214.9	224.3	0.01	1.63±.03	0.77±.12	7.41±.06	1.30±.01	2.01±.07	1.40±.02	1.35±.02	0.26±.03	1.29±.08
30.099	06.7	-131.2	83.8	214.8	224.2	0.02	1.63±.03	0.83±.09	7.37±.06	1.29±.01	2.04±.05	1.41±.02	1.36±.02	0.27±.02	1.27±.08
30.108	08.1	-131.6	86.9	214.9	224.1	0.01	1.65±.03	0.85±.08	7.48±.07	1.31±.01	2.10±.04	1.34±.01	1.26±.01	0.27±.03	1.22±.08
51.897	16.9	-066.1	78.1	236.3	226.7	0.11	1.79±.04	1.35±.16	8.06±.09	1.40±.01	2.17±.09	1.45±.03	1.38±.03	0.37±.04	1.60±.11
51.912	19.5	-066.7	82.9	236.3	226.0	0.12	1.83±.04	1.29±.14	8.10±.09	1.40±.01	2.16±.08	1.48±.02	1.36±.02	0.41±.04	1.64±.12
51.919	20.6	-066.9	85.2	235.6	225.3	0.13	1.81±.04	1.24±.11	8.14±.08	1.40±.01	2.21±.07	1.46±.02	1.36±.02	0.46±.04	1.74±.11
51.926	21.9	-067.2	87.6	214.7	221.8	0.15	1.63±.03	1.11±.07	7.18±.07	1.24±.01	2.02±.06	1.32±.01	1.19±.01	0.48±.03	1.66±.10

H ₂ O	C	INO ₃	HOCl	NO	NO ₂	I	INO ₃	O ₃
19	15	15	15	15	15	16	18	18
1.09±.06	0.44±.92	0.22±.81	2.62	-11.0	2.06	1.18	0.87±.07	6.08±.10
1.57±.01	0.86±.49	0.32±.48	3.52±1.0	2.09±.11	0.88±.01	6.07±.00		
1.48±.03	0.90±.31	0.13±.34	3.11±1.0	2.13±.08	0.90±.03	6.08±.05		
1.79±.05	1.53±.31	0.11±.25	1.72-1.68	0.40±.04	1.53±.03	8.08±.04		
1.791.01	1.47±.33	0.28±.33	1.27:1.81	0.42±.05	1.56±.04	7.95±.04		
1.78:1.04	0.89±.43	0.14±.34	1.72±.66	0.44±.05	1.54±.04	8.01±.05		
1.80:1.01	1.18:1.50	0.19±.35	1.61:1.60	0.53±.06	1.58±.05	8.07±.05		
4.81±.09	0.65±.40	0.02±.35	2.21±1.0	1.39±.07	0.60±.03	5.99±.05		
3.59±.10	1.15±.89	-0.09±.63	149.11±.0	1.18±.13	0.63±.06	6.15±.08		
2.67±.05	0.23±1.0	0.10±.70	2.27±.63	1.40±.13	0.67±.07	6.18±.08		
5.49±.06	0.55±.42	0.08±.29	2.50±.79	1.77±.09	0.28±.03	6.17±.01		
5.00±.07	0.69±.39	0.25:1.29	2.93±.68	1.79±.09	0.31±.03	6.01±.04		
5.42±.07	0.46±.25	-0.03±.20	2.70±.76	1.78±.07	0.29±.00	5.88±.03		
2.96±.06	-0.0x±.64	0.17±.41	3.21±.97	1.92±.11	0.47±.04	6.29±.05		
3.21±.05	0.76:1.39	0.12±.29	3.09±.98	2.00±.07	0.56±.03	6.42±.04		
3.06±.04	0.57±.70	0.05:1.23	3.59±.93	2.20±.06	0.62±.02	6.34±.04		
2.39±.03	0.76±.24	0.28±.21	3.29±.78	2.36±.06	0.67±.02	6.23±.03		















